

Matrix Isolation and Computational Study of the Photochemistry of 1,3,2,4-Benzodithiadiazine

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Photolysis of 1,3,2,4-benzodithiadiazine (**1**) at ambient temperature yields stable 1,2,3-benzodithiazolyl radicals. In order to reveal the mechanism of this unusual transformation, the photochemistry of **1** was studied in argon matrices using IR and UV-vis spectroscopy. A series of intermediates, including four- and five-membered heterocyclic and *o*-quinoid acyclic species, were characterized spectroscopically with the help of quantum chemical calculations. With selective irradiation, these intermediates can be mutually interconverted as well as converted back to the starting compound **1**.

Introduction

An extensive family of polysulfur-nitrogen heterocycles, including both closed- and open-shell structures having an unusually high ratio of heteroatoms (nitrogen and sulfur) to carbon atoms has recently been discovered at the borderline between organic and inorganic chemistry.^{1–4} In particular, the persistent thiazyl (SN) π radicals have emerged as attractive building blocks for molecular magnets and/or molecular conductors.^{2–4} For example, one of the recently synthesized SN π radicals reveals properties of a spin-canted weak ferromagnetic material below 36 K at ambient pressure and below 65 K at high pressure.^{3a} The carrier of the unpaired electron in these radicals is a 2-center-3- π -electron fragment (SN) \cdot , i.e., a sulfur analogue of nitric oxide NO \cdot . It is the same moiety that constitutes the well-known molecular metal and low-temperature superconductor polythiazyl (SN)_x.⁵

The structural versatility of compounds containing the SN fragment and the usually high chemical and thermal stability of thiazyl heterocycles^{2,6} provide opportunities for further investigations of new radicals and materials. For example, benzo-fused SN π radicals such as 1,2,3-benzodithiazolyls (Herz radicals) represent a less studied but potentially very promising class of such compounds.

Typically, Herz radicals are produced by reduction of Herz salts (1,2,3-benzodithiazolium chlorides).⁷ Recently we discovered a new approach to these radicals,⁸ i.e., the thermolysis or photolysis of 1,3,2,4-benzodithiadiazine (**1**), which gives rise to the stable Herz radical, **2**, in quantitative yields (Chart 1). This method has also been successfully applied to prepare a number of new derivatives of radical **2**, including ones that are inaccessible by other pathways.⁸

CHART 1

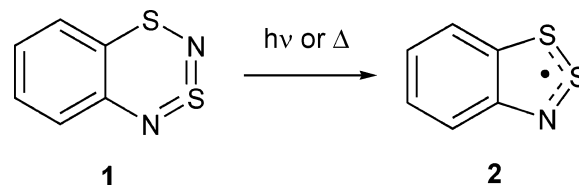
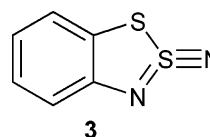


CHART 2



The possibility of generating stable SN radicals photochemically is especially promising in view of new applications of these heterocycles. However, nothing is known about the mechanisms of the thermal and photochemical reactions of 1,3,2,4-benzodithiadiazine (**1**), and apart from a few reports on the preparative photolysis of some sulfur-nitrogen heterocycles designed to isolate only final stable products,⁹ the photochemistry of poly-SN-heterocycles remains largely unexplored.

In our preliminary study,¹⁰ we showed that photolysis of **1** in a low-temperature glassy matrix results in the formation of intermediates which show strong absorptions peaking near 460 nm. As these intermediates are electron paramagnetic resonance (EPR) silent, they must be diamagnetic. Heating of the samples to room temperature results in the disappearance of new absorption band and the formation of an EPR signal typical of the final radical **2**.¹⁰ On the basis of the infrared (IR) spectral changes that were observed upon photolysis of **1** in a cryogenic argon matrix, thiazyl **3**, was proposed as one of the intermediates (Chart 2).¹⁰

However, our subsequent studies revealed that the photochemistry of **1** in argon matrices is very complicated and that several intermediates must be involved in the process. This work is devoted to elucidating the mechanism by which **1** decays on

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photolysis using matrix isolation spectroscopy and quantum chemical calculations

Experimental and Computational Details

Compound **1** was synthesized following the published procedure.^{1a}

Spectroscopy in Argon Matrices.¹¹ A few ground crystals of **1** were placed in a U-tube attached to the inlet system of the cryostat. A mixture of argon with 10% nitrogen (which is added to improve the optical quality of matrices) was flowed through the U-tube and slowly deposited on a CsI window (UV transparent quality, Korth Kristalle GmbH) maintained at ca. 20 K. During deposition the temperature of the U-tube was kept at a fixed value and varied for different samples between -12 and 22 °C.

Photolysis of **1** was effected with a medium-pressure Hg/Xe lamp with appropriate interference and glass filters. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 900 spectrometer (200–1000 nm). IR spectra were measured on a Bomem DA3 interferometer ($4000\text{--}500\text{ cm}^{-1}$) with an MCT detector. The percentage of photoconversion of **1** and the degree of degradation of primary photoproducts on the subsequent irradiation was assessed by integration of individual IR peaks.

Laser Flash Photolysis. A Nd:YAG laser (Spectra Physics LAB-150-10, 266 nm, 5 ns, 30 mJ) was used as the excitation light source. The spectrometer has been described previously.¹² Solutions were prepared in dry spectroscopic grade hexane to an optical density (OD) of about 1.0 at 266 nm. Experiments were performed at room temperature (295 ± 1 K). The sample solutions were changed after every laser shot.

Quantum Chemical Calculations. The geometries and harmonic vibrational frequencies of **1** and presumed intermediates of its photolysis were calculated by the B3LYP^{13,14} density functional method using the 6-31G(d) and 6-311G(df,p) basis sets, with the Gaussian-03¹⁵ suite of programs. All equilibrium structures were ascertained to be minima on the potential-energy surfaces. The harmonic frequencies calculated by B3LYP/6-311G(df,p) were scaled by the factor of 0.98 (for SN-heterocyclic compounds) or 0.97 (for acyclic species) for their use in assigning the experimental IR spectra.

Excited-state energies of **1** and proposed intermediates were calculated at the B3LYP/6-311G(df,p) geometries by the CASSCF/CASPT2 procedure¹⁶ with the ANO-S basis set of Pierloot et al.¹⁷ using the MOLCAS program.¹⁸ In order to arrive at a satisfactory description of all excited states at the CASPT2 level (i.e., remove intruder states) it was necessary to resort to the level-shifting technique,¹⁹ whereby it was carefully ascertained that no artifacts are introduced.

Results and Discussion

It has been shown previously⁸ that photolysis of **1** at ambient temperature yields the persistent radical **2** in nearly quantitative yield ($>95\%$), whereas photolysis of **1** in low-temperature matrices results in the formation of products showing strong absorptions at the blue edge of the visible spectrum.¹⁰ We found that room-temperature laser flash photolysis of **1** in hexane produces a transient UV–vis spectrum (Figure 1, spectrum 1), which nearly congruent with the difference UV–vis spectrum formed upon steady state photolysis of **1** in an argon matrix at 12 K (spectrum 2), although the absorption band around 300 nm is slightly shifted to the red.

On the basis of this similarity we propose that the products formed upon photolysis of **1** in an argon matrix are similar to

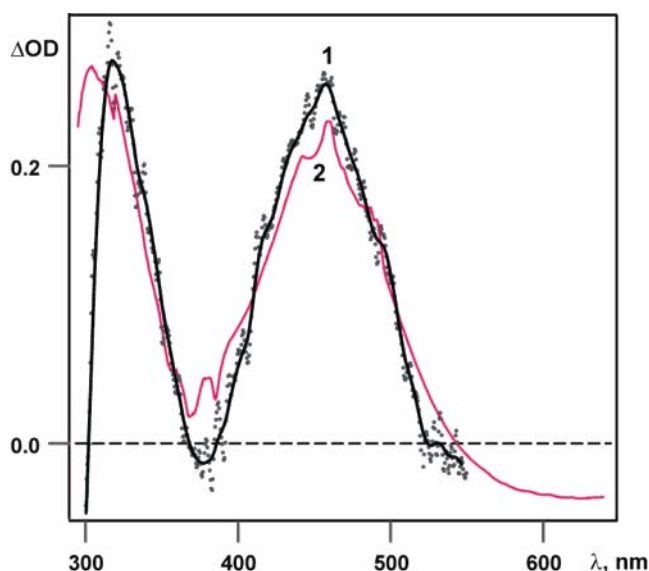


Figure 1. Transient absorption spectrum detected 20 ns after the laser excitation (266 nm, 30 mJ, 5 ns) of 1,3,2,4-benzodithiadiazine (**1**) at 295 K (spectrum 1, averaged over 20 shots, multiplied by 9) and differential absorption spectrum recorded in argon matrix upon irradiation at 313 nm for 5 min (2).

the intermediates of its photolysis at ambient temperature. Therefore, revealing the nature of these species will be invaluable for understanding the mechanism of the formation of radical **2** at ambient temperature.

As we wanted to assign the experimental IR and UV–vis spectra detected upon photolysis of **1** in argon matrices by means of quantum chemical calculations, we began by testing the accuracy and reliability of the methods we intended to use by reproducing the IR and UV–vis spectra of benzodithiadiazine **1**. Figure 2A shows that the calculated IR spectrum of **1** is in very good agreement with the experimental one. Figure 2B shows that some of the UV–vis maxima calculated by the CASSCF/CASPT2 procedure are noticeably shifted to the red, especially the long-wavelength maximum (see also Table S1 in Supporting Information). Nevertheless calculations reproduce the UV–vis spectrum of **1** quite satisfactorily. Therefore it appears that this computational protocol can be used with confidence for spectral assignments of SN heterocycles. Nevertheless, our assignments are based mainly on the IR spectroscopic data.

The quantum yield of 1,3,2,4-benzodithiadiazine photodecomposition at room temperature depends strongly on the excitation wavelength: it is reduced from 0.08 at 313 nm to 3.6×10^{-3} at 365 nm and to less than 3×10^{-4} at 436 nm.⁸ A similar wavelength dependence was observed at cryogenic temperatures. We were unable to decompose **1** using light in the range of 425–700 nm, whereas a comparable amount of **1** was decomposed on excitation at 365 nm for 2 h and at 313 nm for 5 min although the optical densities of the samples at the excitation wavelengths (313 and 365 nm) were similar (0.9 and 1.2). Note that in the spectrum of mercury lamps the intensity of 365 nm line is even higher than that of the 313 nm line.²⁰

The matrix UV–vis spectra recorded after photolysis of **1** at 313 and 365 nm differ noticeably in the visible region (Figure 3, spectra 1 and 2). The latter spectrum is characterized by a broad band with a maximum at 460 nm and a narrow peak at ~ 490 nm. Figure 4 illustrates the corresponding changes in the IR spectrum of **1**. It shows that very similar sets of new peaks, differing only in their relative intensities, are formed upon

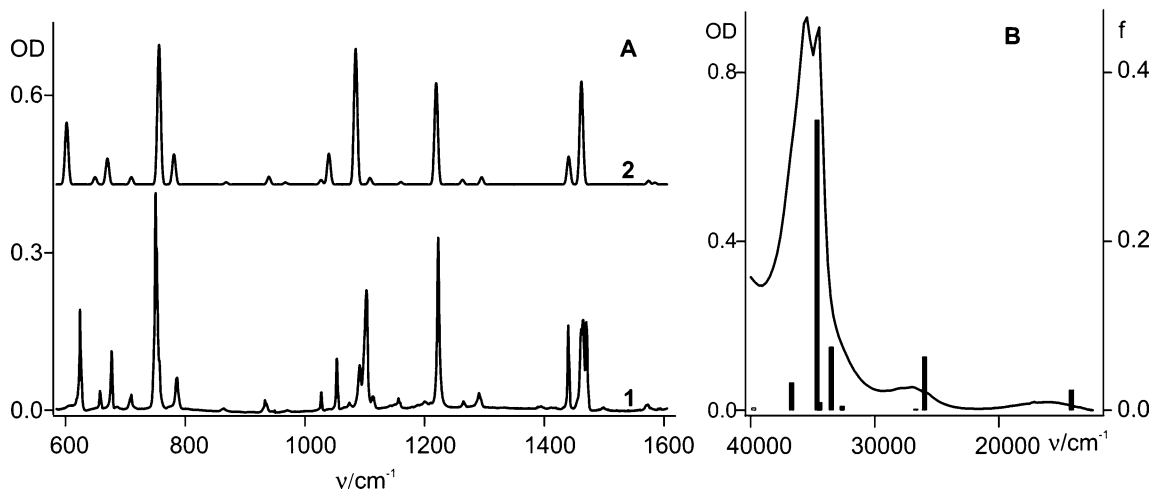


Figure 2. (A) Experimental IR spectrum of 1,3,2,4-benzodithiadiazine **1** in argon matrix at 12 K (1) and its simulation by the B3LYP/6-311G-(df,p) method with a scaling factor of 0.98 (2). (B) UV-vis spectrum of **1** in hexane at 295 K. The vertical bars indicate the positions and oscillator strengths of electronic transitions calculated by the CASSCF(16,12)/CASPT2/ANO-S method at the B3LYP/6-311G(df,p) geometry of **1**.

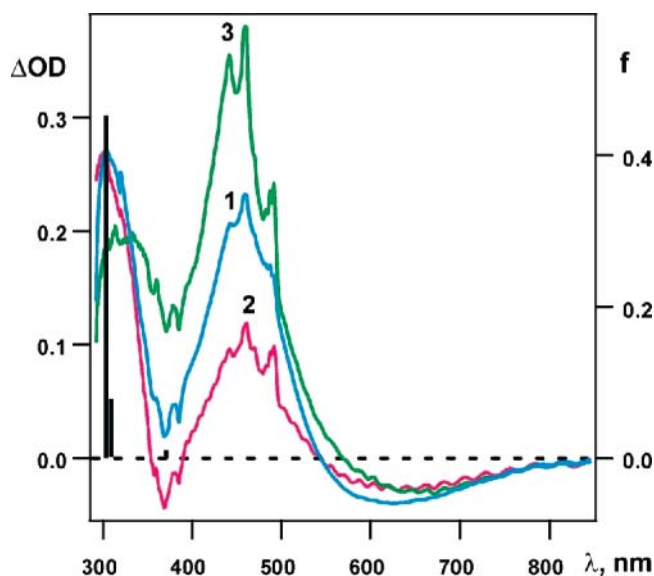


Figure 3. Difference UV-vis spectra detected after photolysis of **1** at 313 nm for 5 min (1) and at 365 nm for 90 min (2) and 20 additional minutes of 313 nm irradiation (3) in an Ar matrix at 12 K. The solid vertical lines indicate the calculated positions and relative oscillator strengths of the electronic transitions of thiazyl **3** (CASSCF (16,12)/CASPT2/ANO-S at the B3LYP/6-311G(df,p) geometry).

photolysis of **1** at 313 (spectrum 1) and 365 nm (spectrum 2). For instance, photolysis at 365 nm gives rise to a more intense peak at 1344 cm^{-1} and slightly less intense peaks at 1492 , 1498 , and 1527 cm^{-1} than photolysis at 313 nm. These differences in the IR and UV spectra of products are indicative of the formation of more than one species on photolysis of **1** in an argon matrix.

Indeed, irradiation at 313 nm of the sample photolyzed previously at 365 nm led to the disappearance of the most intense IR peaks at 1344 and 1443 cm^{-1} (spectrum 3, Figure 4), whereas some other IR bands continued to grow. Figure 4 shows that these intense peaks and also a series of less intense ones (746 , 816 , 931 , 1026 , and 1128 cm^{-1} , spectrum 2) correlate well with the calculated spectrum of thiazyl **3** (spectrum 4). Unfortunately the decrease of the less intense peaks in the spectrum 3 is not evident, although small negative features could be found on detailed examination.

Thiazyl **3** (Chart 2) is an isomer of dithiadiazine **1**, which has the same five-membered heterocyclic moiety as the final

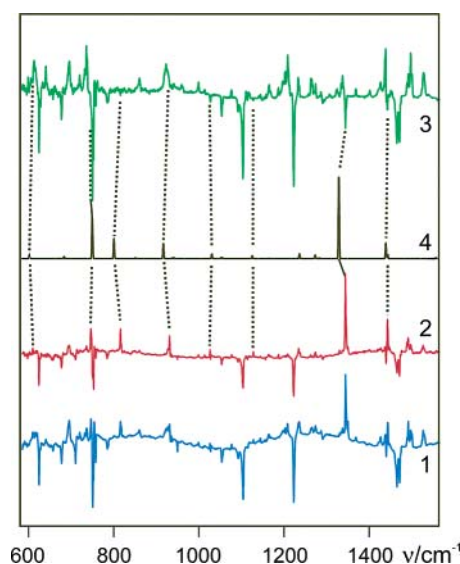


Figure 4. IR difference spectra obtained after photolysis of **1** at 313 nm for 5 min (1), at 365 nm for 90 min (2), and 20 additional minutes of 313 nm irradiation (3) in an Ar matrix at 12 K. (4) IR spectrum of thiazyl **3** calculated by the B3LYP/6-311G(df,p) method with a scaling factor 0.98.

radical **2**. In our preliminary study¹⁰ the intermediate **3** was considered as a nitrenoid species with a structure intermediate between the nitrene $\text{RS}-\text{N}:$ and the thiazyl $\text{RS}\equiv\text{N}$. However the calculated length of the exocyclic SN bond (1.467 \AA) is typical of an SN triple bond.^{21–24} For instance, in thiazyl fluorides $\text{FS}\equiv\text{N}$ and $\text{F}_3\text{S}\equiv\text{N}$ the SN bond length, according to the data from microwave spectroscopy, is equal to 1.448 and 1.416 \AA , respectively,^{21,22} whereas in the thiazylamide anions $\text{R}-\text{N}=\text{S}\equiv\text{N}$ ($\text{R}=\text{Ar}$, Alk), according to X-ray diffraction analysis, it ranges from 1.442 to 1.490 \AA .^{23,24} Note, that the calculated length of heterocyclic SN bond (1.577 \AA) is quite typical of a double bond,^{1a,25} while the heterocyclic SS bond (2.19 \AA) is predicted to be slightly longer than a typical single bond ($2.05 \pm 0.05\text{ \AA}$).²⁶

It is evident from Figure 3 (spectrum 3) that secondary 313-nm photolysis leads to a significant growth of the band intensities in the visible region, whereas the UV band grows much less than initially. We have calculated the UV-vis spectrum of the thiazyl **3** by the CASSCF/CASPT2 method (Figure 3, Table S2) which predicts that this species exhibits

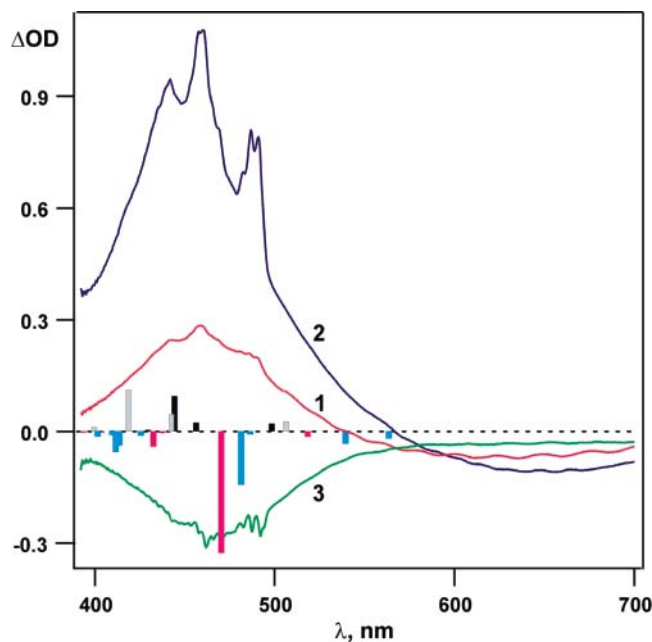


Figure 5. Difference spectra detected upon photolysis of **1** at 313 nm for 10 min (1), 90 min (2), and 30 additional minutes at >515 nm (3) in an argon matrix at 12 K. The vertical bars indicate the calculated positions and relative oscillator strengths of the electronic transitions of the *o*-quinoid acyclic compounds **6** (blue) and **7** (red) and of two rotamers of the four-membered heterocyclic species **8** (black and gray bars, CASSCF(16,12)/CASPT2/ANO-S excited-state calculations at B3LYP/6-311G(df,p) geometries).

strong absorption bands in the near UV region with maxima at 304 nm (with a very high oscillator strength $f = 0.45$) and at 307 nm ($f = 0.075$). Weaker transitions are predicted at 371 nm ($f = 0.01$) and 385 nm ($f = 1.7 \times 10^{-4}$) and a very weak transition at 546 nm ($f = 1.2 \times 10^{-5}$). Therefore, we believe that the absorption band peaking at ca. 300 nm belongs mainly to thiazyl **3** which should contribute negligibly to the visible spectrum, whereas the bands above 400 nm belong to one or several other products (Figure 3). This is why

subsequent photolysis at 313 nm, which decomposes **3**, leads to significant growth of the visible band with the maximum at ca. 460 nm.

The sharp band at 490 nm arises not only on 365 nm photolysis (Figure 3) but more pronouncedly on prolonged irradiation at 313 nm (Figure 5, spectrum 2). Hence this band is probably due to a secondary photolysis product (**4**), which is not yet identified. As the quantum yield of photolysis of **1** at 365 nm is very small, this secondary product **4** appears already during the initial stages of the photodecomposition of **1** at this wavelength (Figure 3).

Subsequent irradiation of the sample at >515 nm leads to the bleaching of the broad band peaking at 460 nm (Figure 5, spectrum 3), although the sharp features at 488 and 492 nm that belong to the secondary product **4** are also affected. In the IR spectrum (Figure 6A, spectrum 2) irradiation at >515 nm leads to the decrease of some peaks and to the growth of others, while the bands of thiazyl **3** (marked by asterisks) remain unchanged. The latter observation agrees with the fact that **3** has no pronounced absorption in the visible region.

It is reasonable to assume that the primary process in the photochemistry of **1** is the cleavage of the SN single bond which leads to the formation of biradical **5** (Scheme 1). The intermediate **5** can undergo cyclization to the thiazyl **3** or relaxation to the *o*-quinoid acyclic products **6** and **7**. Cyclization to a thiazabenzocyclobutene **8** is also possible (Scheme 1).

Interestingly, structures resembling those of **6** and **7** have recently been observed by X-ray diffraction for $X \cdots X (X=S, Se)$ bonded dimers of some 1,2,3-dithiazolyl and -thiaselenazolyl radicals in the solid state.²⁷

The calculated IR spectra of compounds **6–8** correlate satisfactorily with the experimental spectra detected upon irradiation at the indicated wavelengths (Figure 6A). It is clear from Figure 6B that two different products contribute to the doublet at 1492 and 1498 cm^{-1} . The former peak belongs to the product the relative yield of which diminishes upon prolonged photolysis (Figure 6B, spectra 1–3). Two other peaks, at 1498 and 1528 cm^{-1} , belong to the second product, as both of them were bleached on subsequent

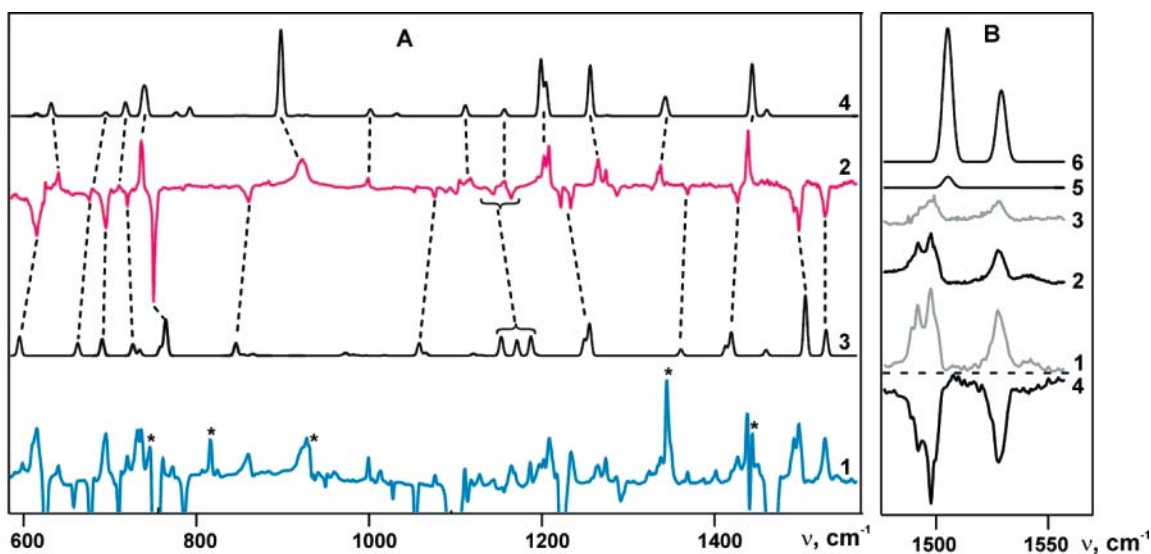


Figure 6. (A) Difference IR spectra detected after photolysis of **1** at 313 nm for 90 min (blue trace 1) and 30 additional minutes at >515 nm (red trace 2) in an Ar matrix at 12 K (the IR peaks of **3** are marked by asterisks). Trace 3 shows the sum of the IR spectra of compounds **6** and **7** in a ratio of 3:1, calculated by B3LYP/6-311G(df,p) (scaling factor 0.97), and trace 4 shows the sum of the IR spectra of a 1:1 mixture of two rotamers of **8**, calculated by the same procedure (scaling factor 0.98). (B) Changes in the region around 1500 cm^{-1} after 10 min (1), 30 min (2), and 60 min of irradiation at 313 nm and finally after 30 min of irradiation at >515 nm (4). Traces 5 and 6 show the calculated spectra of compounds **6** and **7**, respectively.

SCHEME 1: Proposed Scheme of the Primary Processes

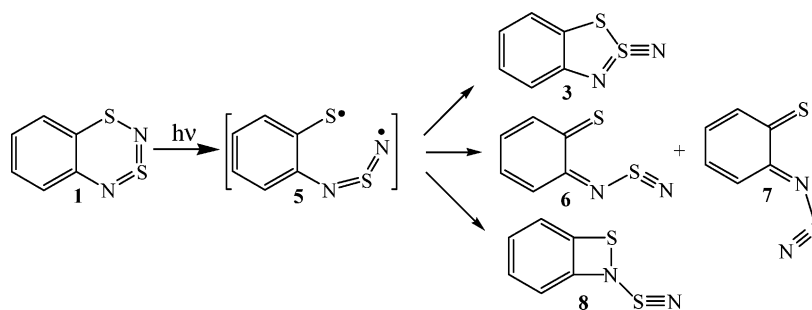


TABLE 1: Vertical Excitation Energies Calculated for *o*-Quinoid Acyclic Species **6 and **7** Using the CASSCF(16,12)/CASPT2/ANO-S Method at the B3LYP/6-311G(df,p) Geometry**

6		7	
λ/nm	$f \times 10^3$	λ/nm	$f \times 10^3$
2315	0.4	1802	0.3
1214	0.4	1203	0.1
701	0.5	674	0.4
564	4.6	519	3.3
540	7.9	478	0.1
487	1.7	471	81.4
482	35.5	438	0.8
426	2.7	433	9.9
414	9.1	404	0.6
412	13.5	394	0.6
410	2.2	384	0.4
402	3.0	379	6.4
385	4.8	349	4.1
366	0.4	337	0.2
323	3.7	333	70.8
320	43.8	317	112.1
318	4.5	297	21.4
296	0.5	284	2.6

TABLE 2: Vertical Excitation Energies Calculated for Four-Membered Heterocyclic Species **8a and **8b** Using the CASSCF(16,12)/CASPT2/ANO-S Method at the B3LYP/6-311G(df,p) Geometry**

8a		8b	
λ/nm	$f \times 10^3$	λ/nm	$f \times 10^3$
499	10.0	507	13.0
457	12.0	444	23.0
444	48.0	419	56.0
430	2.0	400	5.6
365	48.0	348	63.0
319	24.0	322	7.6
316	100.0	314	97.0
275	47.0	273	55.0
274	3.0	270	5.6

for **6**, at 471 nm ($f = 8.1 \times 10^{-2}$) for **7**, and at about 500 and 450 nm for **8a** and **b**. It is obvious that all predicted transitions are close to the maximum of the experimental absorption band at 460 nm. Tables 1 and 2 show that **6–8** have also intense transitions in the near-UV region with maxima at about 300–330 nm ($f = 10^{-2}$ – 10^{-1}). However, their intensities are not so pronounced as that of the main bands of **3** (304 nm, $f = 0.45$; 307 nm, $f = 0.075$).

Note, that **8a** and **8b** are predicted to have also intense transitions at 365 or 348 nm (Table 2). This agrees well with the growth of the absorption around 350–370 nm on prolonged irradiation at 313 nm (e.g., Figure 3, spectrum 3), which is accompanied by the formation of considerable amount of **8** along with **6** and **7** (Figure 4, spectrum 3).

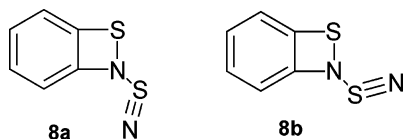
Table 2 and Figure 5 show that the transitions predicted for **8a** and **8b** in the visible region are less intense and shifted to the blue relative to the most intense bands of **6** and **7**. This could be the reason why we observed only a net decrease of the visible absorptions on >515 nm irradiation, although according to the IR spectra (Figure 6A) this decrease was accompanied by the transformation of **6** and **7** to **8**.

The photochemistry of **1** in argon matrices is even more complicated than discussed above. By use of very low concentrations of **1** and effecting excitation at 285 nm, where the absorption of **1** has a maximum (Figure 2B), it was possible to decompose ca. 80% of **1**. The estimation was done using the IR band at 1103 cm^{-1} and the doublet at 1465 and 1471 cm^{-1} . Subsequent 5 min irradiation of the resulting sample at 313 nm leads to a reduction of the IR bands assigned to **3** and **7** but, unexpectedly, to a partial recovery of the IR spectrum of benzodithiadiazine **1** (Figure 7A,B). At that irradiation about 70% of intermediate **3** and ca. 50% of intermediate **7** were decomposed, although only about 25% of the starting material **1** was recovered. Unfortunately the IR spectra of such samples were so weak that only the most intense peaks assigned above to **3** and **7** could be discerned (Figure 7B, spectrum a).

irradiation at >515 nm (Figure 6B, spectrum 4). We assigned the peak at 1492 cm^{-1} to **6** and the latter two to **7**. The other IR peaks that are bleached upon irradiation at >515 nm (Figure 6A, spectrum 2, negative peaks) are reproduced fairly well by the calculated spectra of **6** and **7**, if these species are assumed to be formed in a ratio of about 3:1 (the separate calculated IR spectra of **6** and **7** are reproduced in the Supporting Information, Figure S1).

The IR spectrum formed on subsequent photolysis at >515 nm (Figure 6A, spectrum 2, positive peaks) is in very good agreement with the calculated spectrum of thiazabenzocyclobutene **8**, if one assumes that the two rotamers, **8a** and **8b** (Chart 3), are formed in equal amounts (spectrum 4).

CHART 3



The situation with regard to the assignment of the UV–vis spectra of products **6–8** is less straightforward. The positions and oscillator strengths of the electronic transitions in the spectra of **6**, **7**, **8a**, and **8b** calculated by the CASSCF(16,12)/CASPT2 procedure are depicted schematically in Figure 5 and listed in Tables 1 and 2 (details are in the Supporting Information, Tables S3–S6). Calculations predict that **6–8** have intense transitions in the visible region with maxima at 482 nm ($f = 3.6 \times 10^{-2}$)

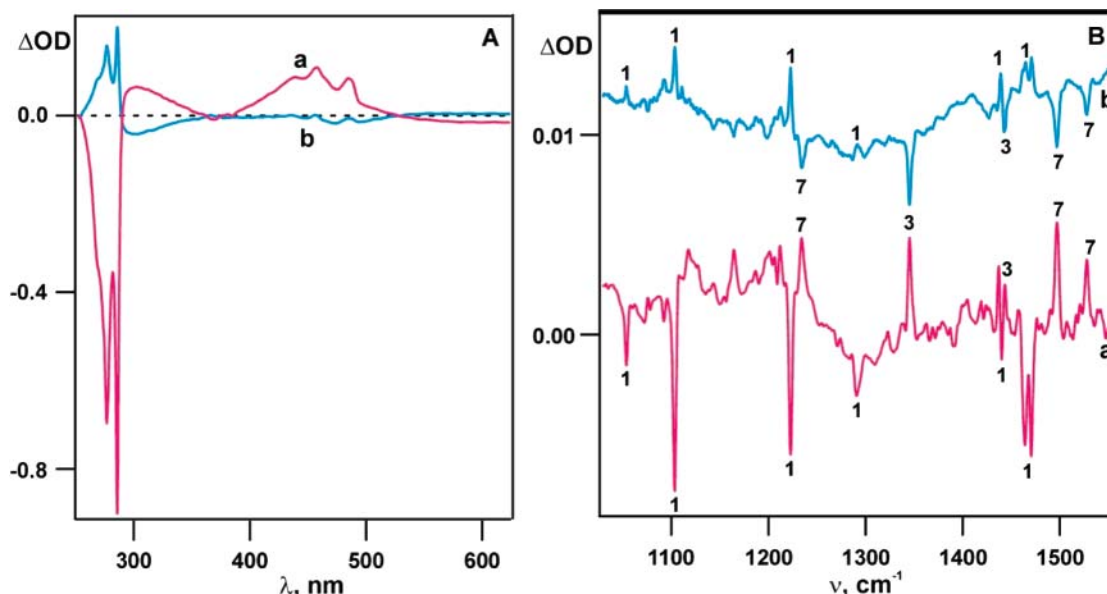
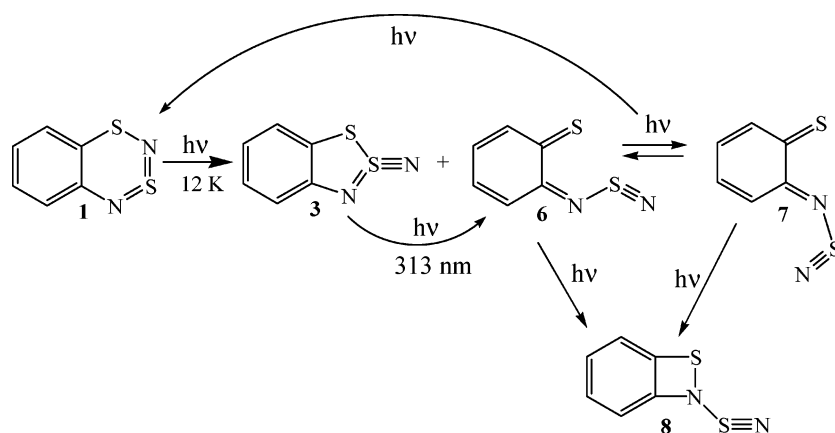


Figure 7. UV-vis (A) and IR difference spectra (B) obtained upon photolysis of **1** at 285 nm for 15 min (red spectra a) and upon subsequent irradiation at 313 nm for 5 min (blue spectra b) in an argon matrix at 12 K. The most prominent peaks are labeled with the numbers of species they are thought to belong to.

SCHEME 2: Photolysis of 1,3,2,4-Benzodithiadiazine in Argon Matrices at 12 K



Additional irradiation at 313 nm for 25 min did not lead to noticeable changes in the UV-vis spectrum. However subsequent irradiation at >375 nm for 30 min led to the recovery of about 20% more **1**. Thus we conclude that the photochemical transformation of **1** is reversible and that, after longer irradiation, a wavelength-dependent photostationary equilibrium is established.

The above-described experiments indicate that at least four products are formed during the initial stages (up to ca. 5% conversion) of the 313-nm photolysis of **1** in argon matrices: a five- (**3**) and a four-membered (**8**) heterocyclic compound and two *o*-quinoid species (**6** and **7**). The formation of **3** and **6** stops after ca. 15–20% of **1** have been bleached. Conversely, the growth of **7** continues, while that of **8**, which is initially very low, increases significantly on prolonged irradiation.

Thus the predominant primary products of the photolysis of **1** in argon matrices are compounds **3** and **6**. On continued irradiation these products undergo further transformation (Scheme 2). In particular, we found (Figure 6A) that compounds **6** and **7** undergo cyclization to **8** even on long-wavelength (>515 nm) irradiation. The same photoreaction should be responsible for the formation of **8** on prolonged irradiation of the sample at 313 nm.

Prolonged irradiation of the sample at 313 nm leads also to the decomposition of **3** and, most probably, to the formation of **6** and **7**, although formation of some unidentified products cannot be excluded. It is obvious that the *o*-quinoid compounds **6** and **7** can interconvert by photochemical *cis-trans* isomerization around the C=N double bond. It cannot be excluded that excitation of **8** at 365 nm leads to S–N bond cleavage and formation of **6** and **7**, along with unidentified product(s). We could not demonstrate this experimentally; however, the absence of product **8** upon 365 nm photolysis of **1** could be an indication of its efficient decomposition.

It is clear from the comparison of the transient absorption spectra obtained at ambient temperature (Figure 1, spectrum 1) with the matrix spectrum (Figure 1, spectrum 2) that at least three intermediates (**3**, **6**, and **7**) are formed upon photolysis at room temperature and these should be accounted for in future analysis of laser flash photolysis experiments.

Figure 8 gives a preliminary account of the thermochemistry of the observed transformations (summary of calculations in the Supporting Information, Table S7). It shows that isomers **3** and **6–8** lie significantly higher in energy than the starting compound **1**, but that they are very close in energy among themselves. In spite of the high exothermicity

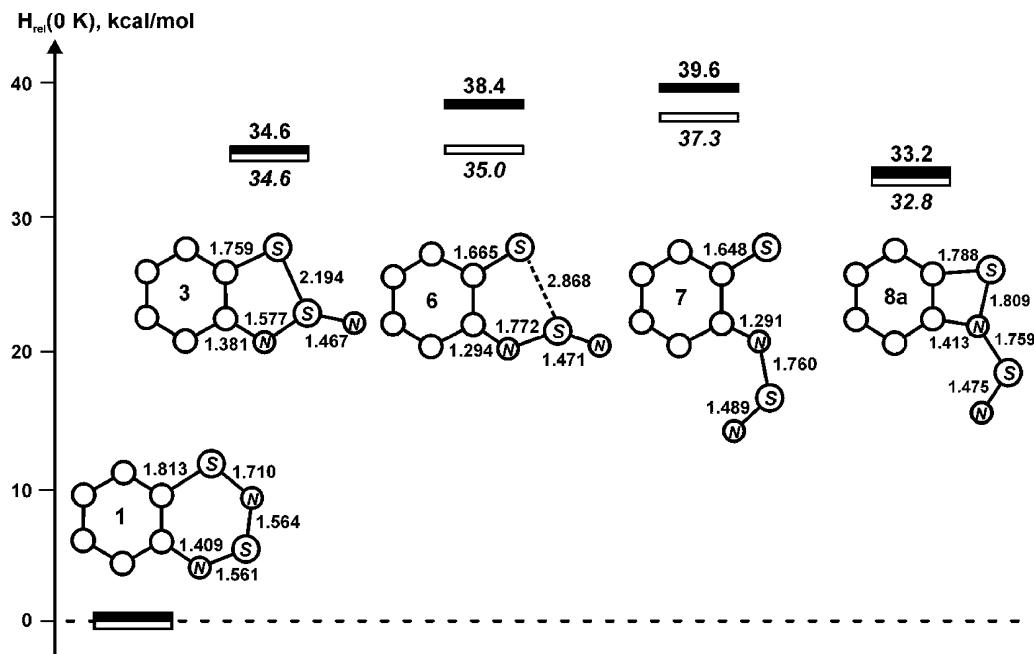


Figure 8. Selected bond lengths (in angstroms) and relative enthalpies (in kcal/mol) of the intermediates involved in the photoisomerization of 1,3,2,4-benzodithiadiazine **1**. The bond lengths and the solid bars refer to B3LYP calculations with 6-311G(df,p) basis set; the open bars refer to the same calculations with 6-31G(d) basis set.

of the reversal of **6** and **7** to **1**, light is needed to induce this reaction in Ar matrices. Calculations predict that the heterocyclic isomers **3** and **8** are somewhat lower in energy than the *o*-quinoid species **6** and **7**. However the latter are unambiguously formed upon photolysis, both at room temperature and in cryogenic matrices. More detailed results of calculations, including activation energies for the interconversion of the different species in their singlet and triplet states and their excited-state reactivity will be presented in a forthcoming publication.

Conclusions

The chemistry of polysulfur–nitrogen (and chalcogen–nitrogen in general) heterocycles is a new area of heteroatom chemistry. Nevertheless, many novel compounds have already been prepared and these are found to feature unusual structures and reactivities, which cannot readily be accounted for within the framework of classical chemical theories. In particular, the mechanistic aspects of polysulfur–nitrogen heterocyclic chemistry remain largely unexplored mainly due to the limited amount of information that can be obtained from conventional spectroscopic techniques (for example, NMR) in this case.

In the present work we have studied the photochemical transformations of 1,3,2,4-benzodithiadiazine in argon matrices at 12 K using IR and UV–vis spectroscopy. Thereby, and with the help of quantum chemical calculations we were able to characterize four- and five-membered heterocyclic species (**8** and **3**) as well as *o*-quinoid species **6** and **7**. We found that all these isomeric intermediates as well as starting compound **1** can be interconverted by irradiation at selected wavelengths.

Acknowledgment. The authors are grateful to the Russian Foundation for Basic Research (Project 04-03-32259), the Siberian Branch of the Russian Academy of Sciences (interdisciplinary project N25), and Swiss National Science Foundation (project No 200020-105217). We thank Professor M.S. Platz at The Ohio State University for the opportunity to use their

laser flash photolysis setup. A.M. and A.Z. thank the Council for the President of Russian Federation Grants for Young Scientists and Their Supervisors (Grant MK-3178.2005.3), and A.M. thanks the National Science Support Foundation (Russia) for a postdoctoral scholarship.

Supporting Information Available: Cartesian coordinates of all stationary points located in this study and details of CASSCF/CASPT2 calculations (text file). UV–vis spectra of dithiadiazine **1**, thiazil **3**, *o*-quinoid acyclic intermediates **6** and **7**, and thiazacyclobutenes **8a** and **8b** calculated by CASSCF-(16,12)/CASPT2 method (Tables S1–S6); calculated IR spectra of **6**, **7**, **8a**, and **8b** (Figures S1–S2); calculations of the formation enthalpy of intermediates **3**, **6**, **7**, and **8** and starting compound **1** by the B3LYP method with 6-31G(d) and 6-311G-(d,p) basis sets (Table S7) (pdf file). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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